

Title: Reducing Acid Soot Emissions

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# **Summary**

## **Background**

In the combustion of high sulfur fuel there is a risk that the process gas temperatures will fall below the sulfuric acid dewpoint. When this occurs the acid in the duct will combine with the fly ash in the duct and scale the duct wall and stack wall with the acid/ash mixture. When the ash dries on the duct walls the acid soot will be emitted into the atmosphere. Depending on the duct material, this soot is may contain acid smuts, iron sulfate and/or chromic acid.

When iron sulfate is emitted into the atmosphere and lands on metal surfaces, it will create a point of corrosion, additionally on non-metallic surfaces it may cause a reddish brown stain. The chromic acid will corrode even non-metallic materials such as fiberglass and plastic.

This paper describes the initial application trials and first stages of reducing the acid soot emissions from the boiler, by determining the heat loss areas, characterizing the acid dewpoint temperature and providing operator feed back with the use of analytical instrumentation.

#### **The Process**

During the combustion of sulfur bearing fuel there is a reaction between the sulfur in the fuel and the oxygen in the flue gas that creates  $SO_2$  and consequently  $SO_3$ . When the free  $SO_3$  in the flue gas combines with water( $H_2O$ ) the reaction forms  $H_2SO_4$ . Dependent on the  $SO_3$  concentration and the  $H_2O$  concentration there may be varying amounts of  $H_2SO_4$ . The sulfuric acid dewpoint of the flue gas is dependent on the  $H_2SO_4$  concentration and hence the acid dewpoint temperature of the flue gas will vary accordingly.

Load, oxygen levels, sulfur in fuel, moisture content of the fuel and boiler cleanliness are also parameters that will affect the acid dewpoint temperature. Since these are difficult to measure, and correlate, on a continuous basis, it is difficult for the operator to understand the effects of the each parameter on the dewpoint temperature. This dewpoint temperature variation, when uncontrolled, could result in the condensation of the sulfuric acid on the metal walls and stack linings resulting in cold end corrosion problems and potential acid smut emissions.



In this case the plant operations evaluated the process conditions, as is, and began to implement a multiple stage process improvements to reduce the effects of the acid soot emissions.

## **Stage One**

#### **Analysis**

One of the major factors for colder flue gas exit temperatures is the efficiency of the cold end heat exchange equipment. Typically the cooling of the gases occurs through the economizer, the air heater and the precipitator area. Additionally this equipment may have air leakage, which adds to the reduction of the cold end temperatures. Furthermore, the ductwork may also have structural deficiencies. Hence, the first targeted area for analysis was the air in leakage possibilities in the duct work expansion joints and seals. In order to pinpoint the probable locations of the leakage thermal image photographs were taken of the duct work from the economizer to the stack. These thermal image photographs showed that there were hot spots on the outside of the expansion joints and duct seams, as well as some duct wall area.

The hot outer areas implies that there may also be cold inner surfaces. Should these surfaces fall below the acid dewpoint, there would be the potential of corrosion and or build up of wet ash on the duct walls.

#### Action

This first stage analysis prompted the plant to seal all of potential areas of heat loss. By doing so they hoped to minimize the corrosion effects on the cold surfaces which also minimized the cooling effects on the process gases, thus allowing for a better control of the flue gas exit temperatures.

## **Analysis**

The second phase of analysis was to profile the air heater inlet temperatures and to control those temperatures above the condensation point of the flue gases.

#### Action

As a result of these temperature profiles it was decided that the combustion air could be pre-heated before it reaches the air pre-heater, thus maintaining a higher temperature on the combustion gas side. Unfortunately, this method would prove to be a costly way to ensure exit gas temperatures are above the acid dewpoint.



## Stage Two

## **Analysis**

After the process gas temperature profiles are complete and all of the necessary mechanical changes are implemented to minimize flue gas heat loss and allow for on line control of the flue gas temperatures, one must begin to understand the and quantify the sulfuric acid dewpoint temperature of the process gas.

There are two methods that were considered for this application. One method was to perform a chemical analysis and use thermodynamic calculations to infer the acid dewpoint temperatures. The second method considered was to measure the acid dewpoint temperatures directly with a sulfuric acid dewpoint meter.

## **Action**

In this particular application it was determined that the best method, for long term, continuous, use would be to directly measure the sulfuric acid dewpoint of the flue gas. This measurement was implemented and performed in an area directly before the air pre-heater section of the process. By measuring the acid dewpoint temperature in this location, they could minimize the effects from air in leakage downstream, testing those points on a periodic basis, for air in leakage and changes in the acid dewpoint.

#### **Analysis**

After the installation of a continuous indication of acid dewpoint, the plant correlated the acid dewpoint temperature to the boiler load, flue gas exit temperature and the type of fuel being burned.

#### Action

From these tests it was determined that if they could maintain their exit gas temperatures above the acid dewpoint temperature, they could prevent the acid soot emissions that were occurring during load changes and prevent cold end corrosion while the boiler was on line.

The following operational changes were then implemented:

Monitor the boiler load and the acid dewpoint temperature. During low load conditions, the acid dewpoint temperature and boiler load curves may correlate to potential acid soot problems or duct wall scaling. To avoid this condition the operator was to either, increase the boiler load or pre-heat the air heater combustion air to raise the stack gas exit temperature.

Since this is a dynamic process the long term solution to the corrosion and smut issues must address the process conditions, the materials of construction and operational procedures.



## **Future Stages**

Having evaluated the temperature profile of the ducts, analyzed the mechanical structure and correlated the acid dewpoint temperature to the boiler load and sulfur in the fuel, the steps listed below are planned for future analysis and action.

## **Process Equipment Cleaning**

The next step will be to perform a cleaning of all of the duct and stack walls and begin to test various methods to reduce the acidity of the flue gas. One possible route being considered is the injection of ammonia, downstream of the precipitator. It is assumed that the ammonia will react with the free  $SO_3$  in the process gas as well as neutralize the acidity of any ash that is left after the precipitator section of the flue gas.

## **Modified Operations/Training**

One key aspect of the current and future process modifications will be implementation of modified boiler operating procedures and the training of boiler operators. This training will ensure that all f the personnel are aware of the requirements to maintain a flue gas exit temperature that is not only acceptable form a boiler load perspective, but also acceptable from a maintenance and environmental perspective.

#### A Note on Duct Wall Material

There have been extensive studies on the proper material for flue gas ducts that will withstand the conditions presented in a high sulfur, corrosive flue gas. Unfortunately, the more expensive metals, Titanium and Hastelloy, seem to provide the best performance, while the coatings, seem to perform no better than the standard duct wall material itself. In any case, if there is still caking or condensing of the acid ash on the walls, and this ash is subsequently emitted to the atmosphere, the ash may take on the form of chromic acid, which will not only corrode metal surfaces, but will discolor any fiberglass material. Hence the changing of the duct wall material may only protect the process from the corrosion end, but not reduce or eliminate the root problem studied here, which is the reduction of the acid soot emissions to the atmosphere.